

AD-A232 071

FREE FILE COPY

2

OFFICE OF NAVAL RESEARCH
Contract N00014-91-J-1045
R&T Code 4132047---02-1

TECHNICAL REPORT NO. 3

Compatibilization of Blends of Crystallizable Polybutadiene
Isomers by Precipitation and by Addition of Amorphous Diblock Copolymer

by

Moiria Marx Nir and Robert E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

February 15, 1991



Reproduction in whole or in part is permitted for any purpose of the U.S. government.

This document has been approved for public release and sale; its distribution is unlimited.

91 2 19 210

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 3			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION MIT, Dept. of Chemical Eng.		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) MIT, Building 66, Room 554 Cambridge, MA 02139-4307			7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (if applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-91-J-1045	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			4132047 02 1		
11. TITLE (Include Security Classification) Compatibilization of Blends of Crystallizable Polybutadiene Isomers by Precipitation and by Addition of Amorphous Diblock Copolymer					
12. PERSONAL AUTHOR(S) Moira Marx Nir and Robert E. Cohen					
13a. TYPE OF REPORT Technical Report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) February 15, 1991	
15. PAGE COUNT 4					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	polymer blends semicrystalline blends		
			emulsified morphologies mechanical properties		
			block copolymers		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A brief summary of the research on compatibilized polymer blends is presented. Of particular significance is the model system of crystallizable polybutadiene isomers: trans 1,4 polybutadiene and syndiotactic 1,2 polybutadiene. Appropriate blending procedures, rapid precipitation from solvent (sometimes in the presence of an amorphous 1,4/1,2 polybutadiene block copolymer) led to a family of blends with attractive mechanical behavior.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

Compatibilization of Blends of Crystallizable Polybutadiene Isomers by Precipitation and by Addition of Amorphous Diblock Copolymer

Maira Marx Nir and Robert E. Cohen

Department of Chemical Engineering
Massachusetts Institute of Technology, Cambridge, MA 02139

Introduction

We studied blends of syndiotactic 1,2 polybutadiene (PBD) and trans 1,4 PBD in order to understand the behavior of binary blends of semi-crystalline materials. The two component homopolymers are non-polar and are isomers of each other, thus these blends constitute a model system for studying structure-property relationships. A second goal of the work was to determine whether amorphous 1,2/1,4 PBD diblock copolymer had the ability to compatibilize blends of the two homopolymers. To prepare the blends, the components were mixed in a mutual solvent and then precipitated in methanol. Compared to spin-casting, the precipitation procedure led to more intimate mixing of the polymers, and thereby enhanced blend properties.

Over twenty years ago, polymer scientists showed that diblock copolymers can compatibilize binary blends of the two homopolymers that comprise the diblock and thus enhance the properties of those blends.¹ The work presented here is an extension of studies of spin-cast blends of amorphous 1,4 and 1,2 PBD homopolymers.² We have added the facet of homopolymer crystallization to the problem. However, rather than add a perfectly matched diblock copolymer where the blocks also have the ability to crystallize, we have chosen to study the behavior of an all-amorphous 1,2/1,4 PBD diblock in semi-crystalline blends of syndiotactic 1,2 PBD and trans 1,4 PBD. The question we can thus answer is whether or not the blocks of the amorphous diblock copolymer have the ability to mix with and emulsify the amorphous portions of the semi-crystalline homopolymers.

Materials and Sample Preparation

Two homopolymers and two diblocks were used in this study and were obtained from the Goodyear Tire and Rubber Company (Akron, OH). Characterization of the homopolymers is discussed below. The first diblock copolymer we studied (referred to as 30/50) has a 1,2 block with MW 30K and a 1,4 block with MW 50K. This diblock copolymer is heterogeneous, i.e. the blocks exhibit microdomain phase separation. The other diblock (referred to as 30/200), the 1,2 block has MW 30K and 1,4 block has MW 200K. This diblock is homogeneous, the blocks do not undergo microdomain phase separation.²

Blends were prepared by stirring 1 gram total of polymer in 50 ml of tetralin (1,2,3,4 tetrahydronaphthalene) at 135°C. After one hour of mixing, the solution was dripped into cold methanol. The precipitate was filtered and dried at room temperature in a vacuum oven until it reached constant weight. The precipitates were then compression-molded in the melt state at 200°C.

Results and Discussion

M_v of the syndiotactic 1,2 PBD is 32K g/mol, M_v of the trans 1,4 PBD is 400K g/mol. The syndiotactic material has a melting point (T_m) of 190°C and a glass transition around 25°C. The trans material melts around 140°C and its T_g is approximately -80°C. Both materials are about 40% crystalline when quenched to 25° from the melt and both exhibit cross-linking and degradation above 200°C. TEM-determined lamellar spacing is approximately 1000 angstroms in the syndio component and 200 angstroms in the trans material.

For all binary blends of syndio 1,2 PBD and trans 1,4 PBD, we found two melting points, thus neither eutecticity nor isomorphism occurs in this system. Theoretical calculations predict that binary blends of syndio 1,2 PBD and trans 1,4 PBD are heterogeneous below and well above the melt region. This prediction was verified by the presence of two glass transitions for all blend compositions tested. The T_m and T_g of the trans component were slightly lowered by the presence of the syndio component, while the syndio component was relatively unaffected by the presence of the trans component. These results occurred presumably because the syndio crystallized first and independently upon cooling from a heterogeneous melt state following the compression-molding process.

Light microscopy and transmission electron microscopy show that the syndio and trans are relatively well mixed for a heterogeneous blend, with domains on the order of about 1 micron. Instron tensile data show that mechanical properties of these blends are intermediate between those of the homopolymers, as opposed to worse than either of the homopolymers as in other phase-separated blends having larger homopolymer domain sizes. However, three binary blend compositions out of five split into layers while undergoing tensile tests.

The intimate mixing in our blends, and the resulting predictable mechanical behavior, seems to be the result of the precipitation procedure. In earlier work with amorphous PBDs prepared by spin-casting, domain sizes were on the order of 5-10 microns and the mechanical properties of their blends were not as good as the component homopolymer mechanical properties.²

A number of blends with either the 30/50 or 30/200 diblock copolymers were also studied. The "ternary" diagram in Figure 1 illustrates the compositions prepared and tested for each of the two diblock copolymers. Rheovibron data show that there are still at least two glass transitions in blends containing both homopolymers with either diblock, therefore our amorphous diblocks did not homogenize the two homopolymers in these blends. Yet the presence of diblock, as well as the type of diblock added, affects the 1,4 PBD glass transition of the blend. Thus the diblock seems to have more of an effect on the trans 1,4 PBD component than on the syndio 1,2 PBD component.

The mechanical properties of the ternary blends indicate that the diblocks give a rubbery character to the blends: Percent strain at fracture increases and stress at fracture, yield stress, and the modulus all decrease as diblock content increases. In two ternary blends with diblock content less than 10%, the layered splitting effect that occurred with the binary blends was seen again, regardless of which diblock was present. Above 10% diblock content, this phenomenon was not observed.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Conclusions

Despite the isomeric nature of the two homopolymers, we have found that binary blends of syndiotactic 1,2 PBD and trans 1,4 PBD are heterogeneous for all temperatures below that at which the materials crosslink and/or degrade. Crystallization and the glass transition of the trans component are affected by the presence of the syndio component but the opposite is not true because syndio crystallizes first from the melt. Yet the syndio and trans are reasonably well mixed, with domain sizes on the order of 1 micron or less, due to the mixing/precipitation procedure. Mechanical properties of these precipitated blends are intermediate between those of the two homopolymers, whereas spin-cast blends often give blends with larger domains and poor mechanical properties.

In ternary blends, the amorphous diblocks do not homogenize the two crystallizable homopolymers, but the glass transition of the trans component is altered by the presence of either diblock. Again, the thermal properties of the syndio component seem to be relatively unperturbed by diblock copolymer. Yet diblock content at or above 10% prevented a layered splitting behavior observed during tensile testing of three out of five binary blend compositions.

Acknowledgements

This project is funded by grants from the Office of Naval Research and the Goodyear Tire and Rubber Company.

References

- ¹ Reiss, G., J. Kohler, C. Tournut, and A. Banderet, Makromol. Chemie. **101**, 58, 1967.
- ² Cohen, R.E., and D.E. Wilfong, Macromolecules, **15**, 370, 1982.

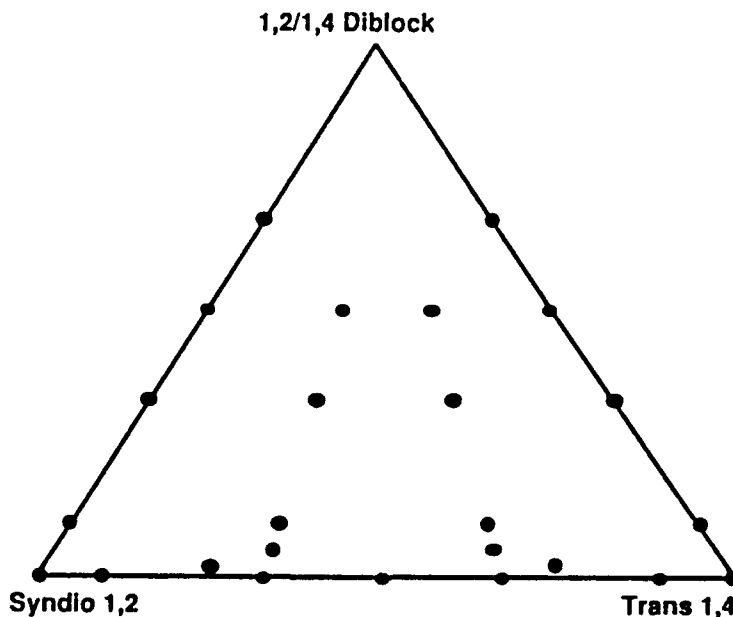


Figure 1: Ternary diagram of samples prepared and studied.